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RESEARCH AND DEVELOPMENT OF
EROSION AND OXIDATION RESISTANT COATINGS
FOR GRAPHITE

First Quarterly Report

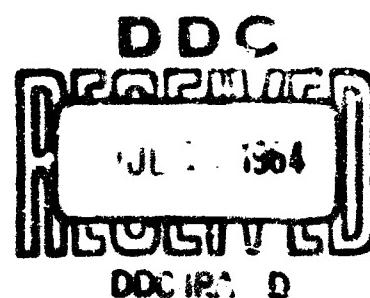
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Conducted for:

Navy Department
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13 July 1964



VECO

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FIRST QUARTERLY REPORT
13 March - 12 June 1964

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FOR GRAPHITE

Conducted for:

Navy Department
Bureau of Naval Weapons

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FOREWORD

This report summarizes the work conducted by Value Engineering Company during the period 13 March 1964 to 12 June 1964.

This program is sponsored by the Navy Department, Bureau of Naval Weapons, and is under the technical supervision of Mr. S. J. Matesky, Code RMMP-23.

ABSTRACT

Attempts were made to increase the ceramic content of the electrodeposited chromium-base cermet coating which had been developed previously. Many plating variables, such as current density, solution temperature, plating solution composition and flashing time and current density, were investigated. The use of a dispersing agent and the effect of different concentrations of ceramic in the plating solution on the amount of ceramic occluded in the coating were studied. It was found that increasing the ceramic concentration to 0.133 ml per ml of plating solution resulted in a coating containing 5% ceramic.

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INTRODUCTION

The primary objective of the research conducted on this contract is to modify and optimize an electrodeposited metal-ceramic coating to protect rocket components in high temperature environments. As a result of work performed under Contract No. N61-0670-c (Final Summary Report dated 22 March 1962) and Contract No. N600(19)58317 (Final Summary Report dated 15 March 1963), a process was developed to deposit chromium-base cermet coatings on graphite substrates. This process utilizes conventional electroplating solutions with ceramic powders suspended in the solution. These ceramic particles are deposited along with chromium metal to form a cermet coating.

There were two major areas of investigation contemplated for this program. One involved the study of conversion reactions for the coating surface. One such conversion coating is a controlled preoxidation.

Previous studies have shown that a controlled oxidation of the cermet coating resulted in the formation of a thin chromium oxide film on the surface of the coating. This film resulted in increased performance which can be attributed to the protective nature of the oxide film as well as to the high melting point of approximately 4150°F of Cr₂O₃ as compared to 3400°F for chromium. A number of procedures would have to be

investigated which would result in an adherent bond between the oxide layer and the chromium cermet. The optimum oxide layer thickness must also be determined. As part of this program, the benefit of forming other compounds such as carbides or nitrides on the surface of the cermet coating would be studied. A very promising development is that of forming spinels. Spinels formed with ZrO_2 or MgO are especially promising. Chromium with 5% MgO has been shown to enhance the oxidation resistance of chromium.

The second major approach for improving the cermet coating is that of employing a controlled diffusion. The "as deposited" coating adheres to the graphite substrate by a mechanical bond and by keying of the coating in the pores of the graphite. This bond is quite strong, but in order to increase the thermal shock resistance properties of the coating, it is felt that it would be necessary to subject the system to a controlled diffusion. This then constitutes the second major effort, namely, the formation of a gradual carbon-chromium diffusion zone.

Another approach to increasing the thermal shock resistance of the coating has been an attempt to locate a grade of graphite which has a coefficient of thermal expansion similar to that of electrodeposited chromium.

The thermal expansion of the ATJ graphite used as a substrate in the coating studies is considerably lower than that of

the cermet coating. This means that as the system is cooled, the coating is placed in tension and develops a tensile crack pattern.

Samples of two grades of graphite having a coefficient of thermal expansion close to that of chromium have been received from Speer Carbon Company. The characteristics of these grades are shown below.

Grade	Apparent Density (gm/cc)	CTE X 10 ⁻⁶ °C (100 - 600°C)	
		With Grain	Against Grain
A-175-e	1.67	5.7	6.1
E-43	1.68	6.0	6.0

The expansion coefficient of chromium is $6.2 \times 10^{-6}^{\circ}\text{C}$. The density of ATJ graphite which is being used in this program is 1.73 gm/cc. ATJ graphite has a coefficient of thermal expansion of $2.19 \times 10^{-6}/^{\circ}\text{C}$ with the grain and $3.42 \times 10^{-6}/^{\circ}\text{C}$ against the grain.

Before embarking on these two studies, it was considered important that every effort be made to increase the amount of ceramic in the coating and use this as a basis for the conversion and diffusor coatings. Consequently, the first quarter of this program has been directed toward a study of various plating variables in order to determine their effect on coating performance and on the amount of ceramic present in the coating. Many plating variables were studied and it was possible to in-

crease the ceramic content of the coating from less than 0.1 to 5%.

There are many variables and combinations of variables which could possibly affect the performance and ceramic content of the coating. Neither time nor funds allowed a study of all these variables. Only those which were considered significant in their effect on coating performance were investigated.

Many texts, reports and references were consulted to assist in outlining the work in this program. A literature search was performed covering the following subjects.

- a. Chromium (properties, compounds, reactions, deposition)
- b. Cermet (formation, composition, properties)
- c. Diffusion (mechanism, conditions)
- d. Graphite (properties, reactions)
- e. Dispersants (operation, types)

The majority of the information obtained will be useful in planning the diffusion and conversion studies. As these studies are conducted, the knowledge obtained from the literature review will be included in the reports describing these studies. Several aspects of aqueous electrodeposition of chromium were revealed which affected some of the plating variable studies.

Electrodeposited chromium from conventional plating solution has a fine network of isolated micro-cracks dispersed throughout its thickness. The cracks in the deposit are supposed to be caused by the large amount of stress developed during initial deposition. The cracking is the result of a decrease in the internal stress with periodic evolution of gas bubbles accompanying this change. When the initial stress is small, few or no cracks occur. These crack-free deposits can be obtained by using high plating solution temperatures, high chromic acid concentrations and high CrO₃ to H₂SO₄ ratios. Although there are fewer cracks formed at the higher solution temperatures the average depth of cracks in the chromium deposit increased with increasing temperature. At a temperature of 100°F, the average crack depth is about 3 microns (0.00012") and at 140°F the average crack depth is about 14 microns. Several graphite samples were coated from plating solutions having a high chromic acid concentration (3 oz/gal) and high temperature (185°F).

The remainder of the coating studies were performed using a "low concentrate" bath which has a nominal chromic acid concentration of 33 oz/gal and 0.33 oz/gal sulfuric acid. This bath is used for obtaining a relatively high hardness deposit, high deposition efficiency and a rapid rate of metal

deposition. As a result, this type of bath is suitable for producing heavy deposits. The "high concentrate" bath, having a nominal chromic acid concentration of 53 oz/gal and a sulfuric acid concentration of 0.53 oz/gal, is used where higher conductivity plus better covering power on more complex parts is required. In addition, this bath is more tolerant to bath impurities and changes in solution composition.

The presence of chlorides in the plating solution at concentrations as low as 0.007 oz/gal is harmful. Chlorides result in loss of efficiency and reduction of covering power. Distilled water was used to prepare all of the plating solutions used in this program so that no contaminants such as chlorides or iron were present.

WORK PERFORMED

During the initial phase, certain plating variables were investigated as a preliminary requirement to optimizing plating procedures and characterizing a reproducible coating. The purpose of this investigation was to produce a coating with the greatest quantity of ceramic particles in the chromium matrix. To this end the following variables were investigated:

- A. Method of Agitation
- B. Type of Ceramic
- C. Particle Concentration (in plating solution)
- D. Dispersant Concentration
- E. General Plating Variables
 - 1. Current Density
 - 2. Bath Temperature
 - 3. Flashing Time and Current Density
 - 4. Chromic Acid and Sulfuric Acid Concentration.

Substrate Samples

Solid Al₂O₃ graphite cylinders 1 inch in diameter and 6 inches long were used in all the coating studies. The cylindrical shape assured a coating of uniform thickness without any buildup at corners. This shape is also beneficial in that no failures will occur at corners or edges during testing. The 6 inch sample was

divided into three sections. X-Ray fluorescence analysis was conducted on one section to determine the ceramic content of the coating, one section was used for oxyacetylene torch evaluation and the third will be used for furnace oxidation tests. By using the same sample, it is more feasible to make a direct comparison of ceramic content and coating performance.

Method of Agitation

To increase the ceramic - metal ratio, three methods of agitation were investigated:

- A. Slow agitation
- B. Vigorous agitation
- C. Periodic agitation

Three graphite cylinders were coated utilizing each of these types of agitation. The ceramic used in this study was tantalum carbide having a particle size less than 2 microns. A section of each sample was submitted for analysis by x-ray fluorescence to determine the quantity of ceramic in the coating. The results of this analysis are tabulated below.

<u>Agitation Method</u>	<u>Sample No.</u>	<u>Plating Bath No.</u>	<u>Wt % Tac</u>
Slow	1	A	.017
	5	B	.004
	9	C	.010
Vigorous	2	B	.010
	6	C	.017
	10	A	.040
Alternate	3	C	.010
	4	A	.009
	8	B	.015

Analysis of variance of these X-ray data indicated that there were no significant differences among agitation methods or plating baths. One explanation for this is that the ceramic particles used had a particle size less than 2 microns as compared to less than 44 microns used in previous studies. Because of this small particle size, any of the agitation methods were able to keep the particles uniformly suspended in the plating solution.

Type of Ceramic

Tests were conducted to determine the relationship between the type of ceramic used in the plating solution and the quantity of ceramic particles occluded in the coating. Zirconium oxide and tantalum carbide were selected for this study. Graphite cylinders were coated from solutions containing 600 ml of each of these ceramics.

X-Ray fluorescence analysis on both type of samples indicated that there were no appreciable difference in the percentage of ceramic in the coatings, both containing less than 0.1%.

Particle Concentration

Samples were coated in plating solutions containing the following concentrations of ZrO_2 :

A. 250 ml

B. 600 ml

C. 1000 ml

These samples were analyzed by x-ray fluorescence and several were analyzed by emission spectrography. The results indicated that all of the coatings contained less than 0.1% ZrO_2 with the exception of the three samples coated in the solution containing 1000 ml. of ZrO_2 . These coatings had a ceramic content of 1.5%, 2.25% and 5%.

Since the plating solution containing 1000 ml of ZrO_2 produced a coating containing such a significantly greater amount of ceramic in the coating, it was decided to determine the reproducibility of these coatings. A new plating solution containing 1000 ml ZrO_2 was prepared and two samples plated from it. Coatings from this second solution contained less than 0.1% ZrO_2 . Further work will have to be performed to obtain a reproducible coating.

Dispersant Concentration

Initial work suggested that the use of dispersants in the plating solution caused an increase in the amount of ceramic occluded in the chromium matrix. The dispersant increases the viscosity of the solution, thus allowing the ceramic particles to remain in suspension for a longer period of time. Another advantage of dispersants is that it imparts a charge to the ceramic which results in a uniform suspension of particles in the plating solution.

Graphite cylinders were coated from solutions containing 100, 140, and 180 grams of dispersing agent to determine the extent to which the ceramic content and the performance of the cermet coating could be improved. All of these solutions contained 250 ml of zirconium oxide. A section of each of these cylinders was submitted for x-ray fluorescence analysis to determine the concentration of ZrO_2 in the coating. The remaining portion of each of the cylinders was evaluated by the oxyacetylene torch test.

There have been a number of problems associated with the use of high concentrations of dispersant in the plating solutions. The addition of the dispersant caused frothing and bubbling of the bath.

Another problem associated with high concentrations of dispersant was that very large quantities of particles were kept suspended in the plating solution. Consequently, when a sample was introduced into the solution, it was immediately covered with ceramic particles, which rendered the surface non-conductive. As a result, there was a very low deposition of chromium.

A number of approaches were investigated to solve this problem. One method was to coat the sample for 5 - 10 minutes before agitating the bath. This allows a very thin film of chromium to be deposited on the sample before the particles become suspended in the plating solution. In addition, an anti-foaming agent was ordered to prevent frothing of solutions containing the dispersant.

X-Ray fluorescence data showed that the ceramic content of the coating was less than 0.1%, thus indicating that the dispersant did not increase the amount of ceramic in the coating.

General Plating Variables

Bath Temperature, Flashing Time and Current Density

In order to obtain an adherent coating on the surface of the graphite substrate, a high current density is used when the sample is first introduced into the plating solution. This is

referred to as flashing. After a specified time, the current is lowered for the duration of the plating cycle. A number of combinations of bath temperature, flashing time, flashing current density and plating current density were investigated to determine if they affect the amount of ceramic in the coating or the coating performance. Three graphite samples were plated under each of the following conditions:

Bath Temperature <u>(°F)</u>	Flashing Current Density <u>(amps/in²)</u>	Flashing Time <u>(min.)</u>	Plating Current Density <u>(amps/in²)</u>
A. 132	8	10	2.5
B. 132	8	10	8
C. 185	8	10	5.2
D. 137	8	60	2.5
E. 132	16	10	2.5
F. 132	16	60	2.5

The ceramic content of all of the coatings produced by these conditions was less than 0.1%.

Bath Composition

In addition to the normal plating solution of 33 oz/gal CrO₃ and 0.33 oz/gal H₂SO₄ which was used in all of the studies, a 53 oz/gal CrO₃ and 0.53 oz/gal H₂SO₄ solution was prepared. Samples were coated from this solution and analyzed by x-ray fluorescence. There was no evidence of increased ceramic content from this solution.

The coatings from this solution, as from the normal solution, contained less than 0.1% ceramic.

Oxyacetylene Torch Test Facility

An oxyacetylene torch test facility was constructed to effectively evaluate the coatings studied in this program. Rotameters were incorporated into the facility to closely control the flow rates of the oxygen and acetylene in order to obtain a reproducible evaluation test.

Test Procedure

It was decided to conduct the torch test by keeping the oxidiser to fuel ratio constant and thereby subject the samples to a constant heat flux rather than testing at a particular specimen temperature. Using a constant heat flux is more representative of what actually occurs in a service environment and this method does not depend on specimen emittance.

The flow rate of oxygen used was 27 scfh and the flow rate of acetylene was 10.8 scfh. A torch tip-to-specimen distance of 15/16 inches was used. This distance was chosen so that the coatings would not fail in too short a time, in which case it would be difficult to differentiate among the coatings. On the other hand, the distance was close enough to make the test relatively severe.

The time to failure was taken as the first appearance of

a hole in the coating. This could be detected by viewing through a dark glass and noting the appearance of any intense hot spot in the coating. An optical pyrometer was used to measure specimen surface temperatures.

Oxyacetylene Torch Test Results

In many cases there was a great scatter of oxyacetylene torch data indicating the need for obtaining a more reproducible coating. However, several conclusions can be drawn from these data. The oxyacetylene test data are shown in Table I.

Dispersant Concentration - Samples coated from plating solutions containing the dispersing agent did not show any improvement in performance. In most cases, in fact, the time to failure of these samples was less than for samples coated from solutions not having the dispersant.

Ceramic Concentration - Samples coated from solutions containing high percentages of ceramic particles failed in less time than samples coated from solutions containing fewer particles.

Samples 26, 29, and 30 contained 5, 2 25 and 1.5 per cent ZrO_2 , respectively, as determined by x-ray fluorescence. The poor performance of these samples can be attributed to two factors. These samples were sectioned, mounted and polished metallographically to study the structure of the cross section. Unlike the other samples which have a uniform coating thickness along their length,

These three coatings were irregular in thickness. Some areas of the coating were less than 0.5 mils while other areas were up to 3.0 mils. Apparently the relatively high ceramic content of the coating causes thickness irregularities. When a ceramic particle is first occluded by the chromium matrix during the plating operation it protrudes beyond the original coating thickness. Consequently there is a greater coating build up in the area of the ceramic particle which is caused by the concentration of current flow to the relatively sharp point of the ceramic particle, the decrease in distance from the anode and the decrease in polarization brought about by the induced stirring of the electrolyte around the particle.

Another possible cause for the poor performance of these relatively high concentration ceramic cermets is the poor adhesion between the chromium and ceramic. This suggests the need for some post coating heat treating operation to increase the bond between the metal and ceramic phases.

Bath Temperature and Current Density - Torch test data indicate that samples coated at 132°F are superior to samples coated at a solution temperature of 185°F.

Flashing Time and Current Density - A flashing time of 10 minutes at a current density of 8 amps/in² resulted in a better coating

than those obtained using a longer flushing time (60 minutes) or higher current density (16 amps/in²)

Bath Composition - No increase in coating performance was obtained by using the "high concentrate" plating solution (1.3 oz/gal CrO₃, 0.53 oz/gal H₂SO₄).

Type of Ceramic - The coating containing the TaC was in no way superior to coatings containing ZrO₂. In view of the low cost of ZrO₂ as compared to TaC zirconium oxide will be used in all future coating studies.

As a result of the x-ray fluorescence analysis and oxyacetylene test the following coating parameter values can be considered optimum and will be used as a basis for further development work.

Type of Ceramic - ZrO₂

Ceramic Concentration - 1000 ml per 9 liters of solution

Solution Concentration - 33 oz/gal CrO₃, 0.33 oz/gal H₂SO₄

Flashing Time and Current Density - 10 minutes, 8 amps/in²

Bath Temperature and Current Density - 132°F, 2.5 amps/in²

Dispersant - None

TABLE I. SUMMARY OF OXYACETYLENE TORCH DATA

Sample No.	Variable Studied	Variable Value	Sample Temperature (°F)	Time To Failure (min:sec)
15	Dispersant Concentration	100 gm dispersant	2730	15:20 NF
16			2900	2:35
17			2820	29:20
19		140 gm dispersant	2900	4:18
24			2730	40:43
27			2710	3:30
31		180 gm dispersant	2780	30:00
33			2860	9:00
35			2700	13:00
20	Ceramic Concentration	250 ml ZrO ₂	2740	36:18
21			2750	27:47
28		600 ml ZrO ₂	2775	9:02
32			2740	60:00 NF
34			2700	2:50
26		1000 ml ZrO ₂	2760	4:00
29			2730	8:00
30			2780	4:40
39	Bath Temperature and Current Density	185 F. 5.2 amps/in ²	2730	43:05
41			2840	13:05
43			2650	5:28
45			2760	22:55
37		132 F. 2.5 amps/in ²	2780	21:00
38			2800	34:30
40		132 F. 8.5 amps/in ²	2840	62:00
42			2780	3:10
44			2720	37:27

57	Flashing	60 min, 8 amps/in ²	2775	7:43
58	Time and		2730	10:23
59	Current			
60	Density	10 min, 16 amps/in ²	2750	5:08
61			2730	5:30
			2760	8:37
53	Bath	53 oz/gal CrO ₃ ,	2760	28:19
55	Composition	0.53 oz/gal K ₂ SO ₄	2760	9:38
50	Type of	TaC	2780	2:46
69	Ceramic			
70	Ceramic	1000 ml ZrO ₂	2800	3:22
72	Concentration		2750	36:01
			2870	12:44
71	Temperature	185 F, 5.2 amps/in ²	2770	15:30
73	and Current	(using 1000 ml ZrO ₂)	2800	27:20
75	Bias			
76	Dispersant	100 gm dispersant	2740	2:46
78	Concentration	(using 1000 ml ZrO ₂)	2860	4:13
			2800	8:38

NF - No Failure

FUTURE WORK

Investigations performed during the first three months have shown that the ceramic content of the cermet coating could be increased from less than 0.1. to the 1.5 to 5 per cent range. The reproducibility of the coating, however, is poor. One of the tasks during the second quarter, therefore, is to briefly study the conditions which will result in coatings have a consistently high ceramic content.

The major effort during the second quarter will be a study of conversion reactions and diffusion operations necessary to improve the performance of the coating. The first conversion reaction to be studied will be a controlled oxidation. A pre-oxidized coating has been shown to be superior to the "as deposited" coating. The optimum temperature and time to give an adherent and dense oxide layer will be determined. The temperature, time and furnace atmosphere to produce the optimum graphite-cermet diffusion zone will also be determined.